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<p>(21) International Application Number: PCT/BR94/00019 (22) International Filing Date: 12 May 1994 (12.05.94) (30) Priority Data: PI 9301831 13 May 1993 (13.05.93) BR (71) Applicant (for all designated States except US): POLIBRASIL S.A. INDÚSTRIA E COMÉRCIO [BR/BR]; Estrada da Vila Sonia Maria, 2700, Mauá, SP (BR). (72) Inventors; and (75) Inventors/Applicants (for US only): PASSOS CONI JÚNIOR, Osvaldo, Luiz [BR/BR]; Apartamento 301, Rua Marujos do Brasil, 19, B. Nazaré, Salvador, Bahia (BR). SOARES BOAVENTURA FILHO, Jaime [BR/BR]; Apartamento 1607, Avenida Princesa Isabel, 526, Barra, Salvador, Bahia (BR). FABIAN FERNANDES, Helenice, Maria [BR/BR]; Quadra B-03, Avenida Praia de Pajussara, Vilas do Atlântico, Lauro de Freitas, Bahia (BR). ILLIPRONTE, Waldir [BR/BR]; Apartamento 34D, Rua Dom Armando Lombardi, 80, Jardim Guedala, Butantã, SP (BR). (74) Agent: DANNEMANN, SIEMSEN, BIGLER & IPANEMA MOREIRA; Rua Marquês de Olinda, 70, Botafogo, 22251-040-Rio de Janeiro, RJ (BR).</p>	<p>(81) Designated States: AT, AU, BB, BG, BR, BY, CA, CH, CN, CZ, DE, DK, ES, FI, GB, HU, JP, KP, KR, KZ, LK, LU, LV, MG, MN, MW, NL, NO, NZ, PL, PT, RO, RU, SD, SE, SK, UA, US, UZ, VN, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG). Published With international search report.</p>	
<p>(54) Title: HIGH MELT STRENGTH POLYPROPYLENE, CONTINUOUS PROCESS FOR THE PRODUCTION THEREOF, AND MOLDED ARTICLE</p> <p>(57) Abstract</p> <p>A high melt strength polypropylene of wide or bimodal molecular weight distribution is described, which imparts to the product rheological characteristics such as it can be formed in machines normally used for resins such as polystyrene. Molded articles produced from the inventive polypropylene are also described. Also described is a continuous process for producing the high melt strength polypropylene which is obtained in the presence of a Ziegler-Natta type catalyst system, using at least two polymerization vessels connected in series, the control of the molecular weight being effected by the addition of discrete amounts of a molecular weight regulator, such as hydrogen, to at least one of the various polymerization vessels, so as to obtain in the first polymerization vessel a portion of higher molecular weight and in the following polymerization vessels, polymer portions of lower molecular weight, whereby the total polymer shows a wide or bimodal molecular weight distribution, which impart to the product interesting rheological properties.</p>		

Specification of the Patent of Invention "HIGH MELT STRENGTH POLYPROPYLENE, CONTINUOUS PROCESS FOR THE PRODUCTION THEREOF, AND MOLDED ARTICLE "

5 FIELD OF THE INVENTION

This invention relates to a high melt strength polypropylene with a molecular weight distribution which leads to rheological characteristics that renders it especially suited for thermoforming, sheet forming and blow molding. More specifically, the present invention relates to a polypropylene with characteristics derived from its high melt strength which
10 enables the production, by molding it pure or compounded with mineral fillers, of molded articles with excellent appearance, while of inferior cost as compared to those presently molded from polystyrene.

The present invention also relates to a continuous process for producing the inventive high melt strength polypropylene. More specifically, the present invention relates to a
15 continuous propylene polymerization process in the presence of a Ziegler-Natta catalytic system, the process making use of at least two polymerization vessels connected in series, while discrete amounts of a molecular weight regulator such as hydrogen are added to at least one of the polymerization vessels to produce high melt strength polypropylene.

20 BACKGROUND OF THE INVENTION

Although polypropylene is a widespread, cheap and well-known plastic material, its high crystallinity requires special machinery for its processing, such as accurate and expensive to produce a polypropylene which could be processed in machinery not provided for with stringent, accurate temperature controls. A high melt strength polypropylene would
25 correspond to such requirements. Several documents of the technical and patent literature report the search for such a high melt strength polypropylene.

European Patent EP 98968 describes a polypropylene obtained by polymerizing propylene or propylene and ethylene, in several steps or stages in the presence of a catalyst which comprises a titanium trichloride composition, an aluminum compound and a molecular
30 weight regulator, characterized in that the ultimate or total polymer which comprises a higher molecular weight polymer and a lower molecular weight fraction has a melt index (MI) of from 0.03 to 2.0 g/10 min; while between this melt index and the HMI (determined at 10.8 kg/10 min, 230.°C) obtained under a load 5 times higher than that used for the MI, there is the

Compound (IV) has the general formula $Al R_a R'_n X_{3-(a+n)}$ and the molar ratio (V:III) of the aromatic carboxylic acid ester to the solid product (III) is in the range of 0.1 to 10.0. In this polymerization, the amount of propylene polymerized at the first stage is adjusted so as to constitute 35 to 65% by weight based on the total amount polymerized and, in the second stage et seq., it is controlled so as to constitute 65 to 35% by weight based on the total product. The intrinsic viscosity values of the respective polymer portions are also adjusted in order to satisfy the equation

$$3.0 < n_H - n_L < 6.5 \quad (1)$$

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wherein n_H is the intrinsic viscosity of the higher molecular weight portion and n_L is the intrinsic viscosity of the lower molecular weight portion, the portions being those formed in the first stage and those formed in the second and subsequent stages.

In the preferred embodiment of EP 98077, the amount of polymer portion from the first stage (A) is nearly equal to that from the second stage (B) and concretely the amounts are both in the range of 35 to 65% by weight based on the total weight of (A) and (B), preferably 40 to 60% by weight. If the ratio of the amounts of (A) and (B) exceeds the above-mentioned range, the resulting polypropylene does not present sufficient melt flow properties, the kneading effectiveness at the time of granulation is insufficient and it is not only difficult to obtain a homogeneous molded product, but also the extent of improvement in the melt viscoelasticity is small. Further, the difference between the molecular weights of the two portions should be within a range of definite values as described above in equation (1), this polymerization condition being therefore fulfilled by adjusting the concentration of gas phase hydrogen. The process disclosed in EP 98077 involves batch polymerization in bench scale.

In US patent 4,760,113 a continuous process for producing a high melt viscoelastic ethylene-propylene copolymer which produces a block ethylene-propylene copolymer having superior physical properties suitable for sheet molding and blow molding and capable of producing large-size molded articles is provided. The process comprises feeding ethylene and propylene in a weight proportion of 0.5% of ethylene based on the total of propylene and ethylene, into three or more polymerization vessels connected in series, to carry out continuous polymerization step (1) and successively feeding ethylene and propylene in a weight proportion of 10-100% of ethylene based on the total of ethylene and propylene into one or more polymerization vessels, to carry out continuous polymerization process (ii); (b) feeding the

present various drawbacks, either due to the industrial implementation of such processes, for example when they are carried out batchwise, as is the case for EP 96968 and EP 98077, or either due to the catalyst complexities or still, due to the inherent difficulties of a continuous copolymerization process using pressure drop vessels and an additive to reduce the catalyst activity as in US 4760113. Moreover, in order to obtain better properties of the end product, it is advisable to have a weight proportion of at least 35%, and even 40 to 50%, of the higher molecular weight product in the total polymer. Thus, a process is needed for the homo or copolymerization of propylene in the presence of a Ziegler-Natta type catalyst which would produce a high melt strength polypropylene of improved processing behavior, such process being provided for by the present invention.

Therefore, an objective of the present invention is a polypropylene of high melt strength, with rheological properties such that it is especially suitable for several forming techniques, being even a substitute for polystyrene in several applications.

Another objective is a high melt strength polypropylene, suitable for producing molded articles of excellent shape and appearance which can be transformed in machinery normally used for processing more rigid resins, of less stringent temperature requirements.

Another objective of the present invention is a continuous process for preparing polypropylene and optionally its copolymers having wide or bimodal molecular weight distribution, wherein the molecular weight is controlled so as to obtain polymer portions of different molecular weights, wherein the ratio of the molecular weights of the portions produced in the first and in the further reactors lead to a high melt strength polypropylene.

Another objective is still to improve the thermal and mechanical properties of polypropylene molded articles by incorporating mineral fillers such as talc and calcium carbonate thereto.

SUMMARY OF THE INVENTION

This invention refers to a polypropylene of wide or bimodal molecular weight distribution which confers excellent thermoforming characteristics to the polymer product, whereby it is uniformly distributed in the final molded article which results in excellent shape and appearance.

The inventive propylene is still distinguished by the fact that its rheology makes it possible the processing thereof in more simple machinery with less accurate temperature control means than those normally used for molding polypropylene.

being kept always at 180°C. These Figures show the dependence of three viscoelastic variables, the Storage Modulus G' , the Loss Modulus G'' and the complex viscosity η^* on the shear rate as measured by means of an oscillatory effort made on the sample.

FIGURE 5 illustrates a comparison between the viscoelastic data for two commercial polypropylenes, one of them indicated as Commercial PP 1 having Melt Flow Index (M.F.I.) around 1.6 while the other one indicated as Commercial PP 2 has M.F.I. around 2.2, both Indices being determined at 230°C and 2.16 kg. Corresponding curves for the features of both samples show the same general shape, with one curve slightly displaced as to the other one. This behavior indicates similar processability for both polypropylenes, their thermoforming properties being inferior to the products of the invention.

FIGURE 6 compares the viscoelastic behavior of samples produced according the Example 1 of the invention and Commercial PP 2. In this case correlation curves for the viscoelastic properties for the samples of the various polypropylenes show a significantly different behavior. Thus, while the Loss Modulus G'' and the complex viscosity η^* for Example 1 of the invention are higher at lower frequencies, this behavior is changed at high frequencies. As regards the Storage Modulus G' , for Example 1 this parameter is significantly higher at low frequencies, while at higher frequencies, the behavior of both Example 1 and commercial PP 2 is similar concerning this parameter.

FIGURE 7 illustrates viscoelastic data for a polypropylene produced according to Example 2 of the invention as compared to commercial PP 2.

FIGURE 8 shows viscoelastic data for the polypropylene of Example 3 as compared to a commercial PP. Higher values for Storage and Loss Modulus of the inventive product indicate a better thermoformability. However, contrary to the product of Example 1, the figures for complex viscosity are high as compared to the commercial PP, indicating inferior extrusion ability.

FIGURE 9 shows viscoelastic data for the polypropylene of Example 4 as compared to a commercial PP. As indicated in Figure 9, the product of this Example does not show the superior properties of the inventive polypropylenes.

DETAILED DESCRIPTION

The process for preparing the high melt strength polypropylene according to the invention comprises the steps of:

- a) providing at least two polymerization vessels connected in series;

by those skilled in the art. The catalyst should be fed to the first polymerization vessel of the series of the at least two polymerization vessels and, thereafter, the catalyst solids are continuously transferred to each further polymerization vessels together with the remaining reaction mixture, while being withdrawn from the last polymerization vessel whereby the solid catalyst particles are coated with the polymers formed thereon in each respective polymerization vessels.

In order to obtain the desired results, the propylene monomer is normally introduced at different pressures in each of the reaction vessels. Usually it is introduced under a pressure of at least 6.0 kg/cm² G in the first polymerization vessel, which thereafter successively decreases of at least 0.1 kg/cm² G in each of the following polymerization vessels. Although the homopolymer of polypropylene prepared according to the process of the invention shows excellent properties, other olefins such as ethylene may also be added to the polymerization step.

Also according to a preferred embodiment of the invention, hydrogen is used as the molecular weight regulator and is fed into at least one of the polymerization vessels, the molar ratio thereof being adjusted so that at the end of the polymerization process, two polymerization portions of different molecular weights are produced, that is to say, a broad or bimodal distribution of molecular weights is obtained so as to produce a final product of suitable rheological properties. The best mode to effect such broad or bimodal molecular weight distribution is by injecting hydrogen into at least one of the polymerization vessels at a molar ratio of the hydrogen flow rate to the propylene flow rate in the range of zero to 0.0002 in the first of the series of polymerization vessels and between 0.0015 and 0.0035 in the following vessels.

The polypropylene obtained according to the above described method presents a higher molecular weight portion and a lower molecular weight portion, the former showing a MI < 1.0 g/10 min as measured at 190 °C/ 10 Kg. The total polymer has a MI < 3.0 g/10 min as measured at 230 °C/ 2.16 Kg. The polymerization is normally adjusted to produce 10 to 35% by weight of the higher molecular weight portion and 65 to 90% by weight of the lower molecular weight portion and preferably the higher molecular weight portion constitutes 15 to 30% by weight of the total polymer. But the best results are achieved when the proportions of the polymerized produced fractions are controlled in each vessel and generally, the quantity of the polymer obtained from the first of the series of said at least two polymerization vessels is adjusted to render a concentration of 10 to 35% by weight of the total polymer produced in the

polymer product was discharged from the last polymerization vessel of the series, it was treated with an aqueous isopropyl alcohol solution in order to eliminate catalyst residues. Propylene homopolymer was obtained at a rate of 10,000 kg per hour. Polymer physical properties are listed in Table 1.

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EXAMPLE 2

In this Example catalyst, temperature and pressure were as in the previous Example. However, propylene flow rates into the various polymerization vessels R1, R2, R3 and R5 were respectively 4,200; 4,100; 2,400 and 20,0 kg/hour; the hydrogen molar concentration dissolved in propylene to be added to R1 was 0.02 mole% while in polymerization vessels R2 to R5 it was 0.2 mole%. The reaction was run during 12 hours; after completion of the reaction and treatment of the polymer with isopropyl alcohol the yield of propylene homopolymer was 10,000 kg per hour.

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EXAMPLE 3

In this Example catalyst, temperature and pressure were the same as those employed in the polymerization of Example 1. However, propylene flowrates in the various polymerization vessels from R1 to R5 were respectively 5,000, 3300, 2,400, 20 and 20 kg/hour; the hydrogen molar concentration dissolved in the propylene added to R1 was 0.0044 mole % while in the polymerization vessels R 2 to R5 it was 0.3 mole %. The reaction was run during 12 hours; after completion of the reaction and treatment of the polymer with isopropyl alcohol the yield of propylene homopolymer was 10,000 kg per hour.

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EXAMPLE 4

In this Example catalyst, temperature and pressure were the same as those employed in the polymerization of Example 1. However, propylene flowrates in the various polymerization vessels from R1 to R5 were respectively 2,200, 5100, 3,400, 20 and 20 kg/hour; the hydrogen molar concentration dissolved in the propylene added to R1 was 0.02 mole % while in the polymerization vessels R2 to R 5 it was 0.2 mole %. The reaction was run during 12 hours; after completion of the reaction and treatment of the polymer with isopropyl alcohol the yield

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EXAMPLE 5

In this Example, both a commercial polypropylene and the inventive polypropylene were molded in a Brown HD type engine normally used for the thermoforming of polystyrene. This engine is provided with two furnaces, a superior one and an inferior one. In the superior furnace temperatures were 180, 170 and 170°C. In the inferior furnace temperature was 170°C. The molded sheet had 0.8 mm width, the engine productivity being 8.5 cycles/minute. It could be seen that the inventive polypropylene yielded molded articles of smooth surface and perfect grooves using cycles a bit longer than those of polystyrene (12 vs 8.5 cycles/min) while for a commercial polypropylene, either it was not moldable at all in such a machine, or the molded article did not have good appearance and shape. Thus, the viscoelastic behavior exhibited by the polypropylene of the invention at low frequencies leads to the conclusion that the polypropylene of the present invention shows superior thermoforming qualities. Moreover, the polypropylene of the present invention shows equally better extrusion ability in view of it having lower viscosity at high shear rates (high frequencies). The excellence of the inventive product derives from the combination of excellent thermoforming ability and excellent extrusion ability.

EXAMPLE 6

In the same thermoforming machine and under the same conditions as in Example 5, a composition was molded which contained the inventive polypropylene plus 20 wt% of calcium carbonate. The so molded articles had excellent appearance and heat resistance, without deformation. In this case, the productivity of the thermoforming machine is comparable to that obtained in the processing of polystyrene, that is, 11 cycles/min for the filled polypropylene and 12 cycles/minute in the case of polystyrene. This Example demonstrates the excellence of the polymer product of the invention, that is, a propylene polymer processed in machines and cycles normally used for polystyrene.

EXAMPLE 7

This Example refers to the "spiral flow test": polypropylene samples (commercial and inventive) of various Melt Indices are melted and passed under pressure within a loop-shaped

CLAIMS

1 A high melt strength polypropylene comprising a portion of higher molecular weight and a portion of lower molecular weight, the total polymer having a melt index M.I. < 3.0 g/10 minutes as measured at 230 °C/2.16 kg, and in which the higher molecular weight portion has a melt index M.I. < 1.0 g/10 minutes as measured at 190 °C/10 kg, the polymer comprising from 10 to 35 wt% of the higher molecular weight portion and from 65 to 90 wt% of the portion of lower molecular weight.

2 A polypropylene according to claim 1, wherein the portion of higher molecular weight constitutes from 15 to 30 wt% of the total polymer and the portion of lower molecular weight constitutes from 70 to 85 wt% of the total polymer.

3. A polypropylene according to claim 1, wherein the polypropylene is compounded with from 5 to 40 wt% of mineral fillers such as calcium carbonate, talc, glass fiber and 0.1 to 0.5 wt% of an antioxidant and 0.1 to 0.5 wt% of an antistatic.

4 A process for producing a high melt strength polypropylene comprising the continuous polymerization of propylene in the presence of a Ziegler-Natta type catalyst system and a molecular weight regulator, the molecular weight regulator being used in an amount sufficient so as to produce a polypropylene comprising 10 to 35 wt% of a portion of higher molecular weight and 65 to 90 wt% of a portion of lower molecular weight, the total polymer having a melt index M.I. < 3.0 g/10 minutes as measured at 230 °C/2.16 kg, and in which the higher molecular weight portion has a melt index M.I. < 1.0 g/10 minutes as measured at 190 °C/10 kg.

5. Process according to claim 4, comprising the steps of:

- a) providing at least two polymerization vessels connected in series;
- b) feeding the Ziegler-Natta catalyst into the first vessel of said at least two polymerization vessels;
- c) feeding propylene into each polymerization vessel in such a manner that the pressure under which the propylene is fed decreases from the first to the further vessels;
- d) introducing the molecular weight modifier into at least one of said at least two vessels in a sufficient amount to provide the bimodal molecular weight distribution in the resulting product;
- e) successively transferring the catalyst and the resulting polymerization reaction mixture from the first to each further polymerization vessels, while the products polymerized in each polymerization stage are added to and formed on the same catalyst solids, which thereafter

FIGURE 1

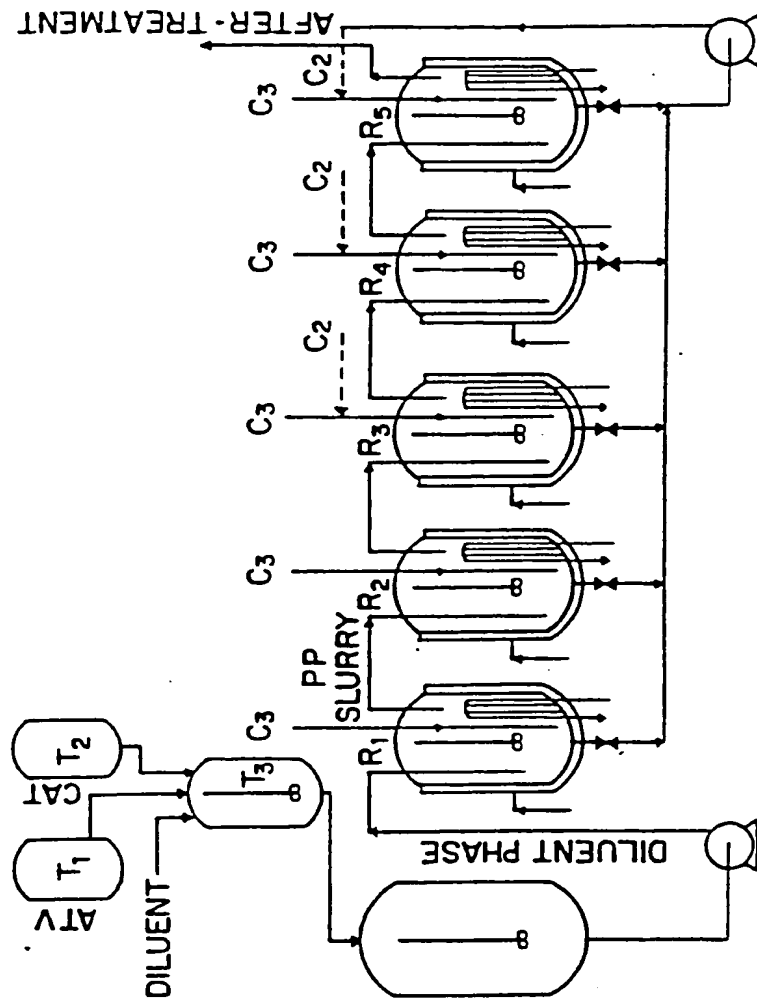
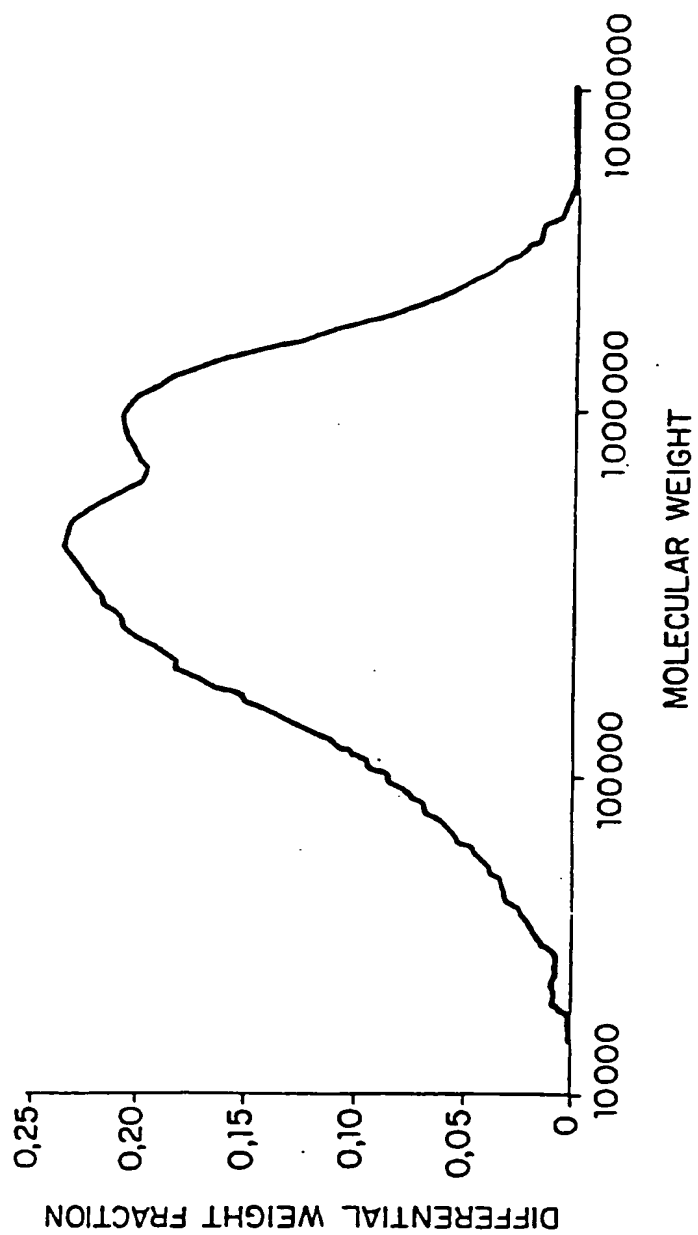
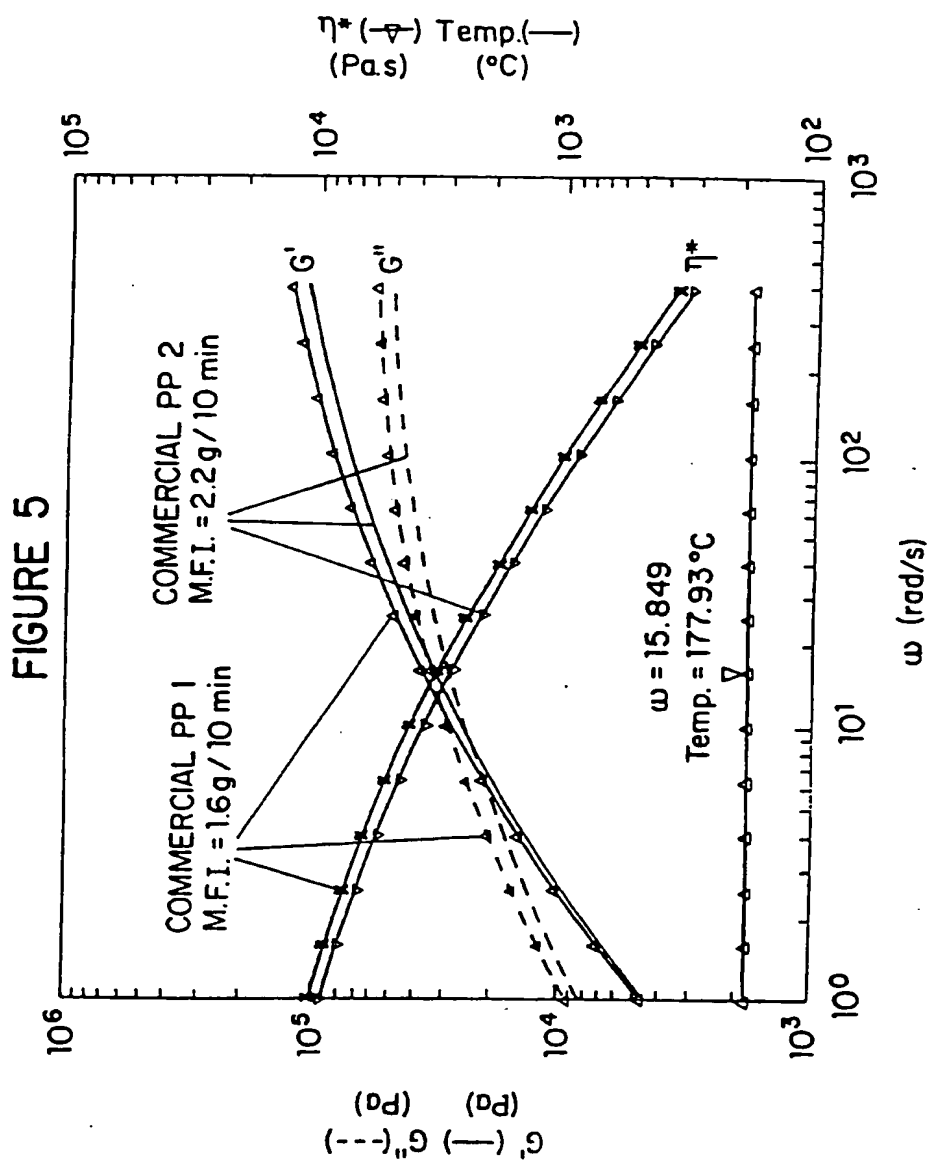
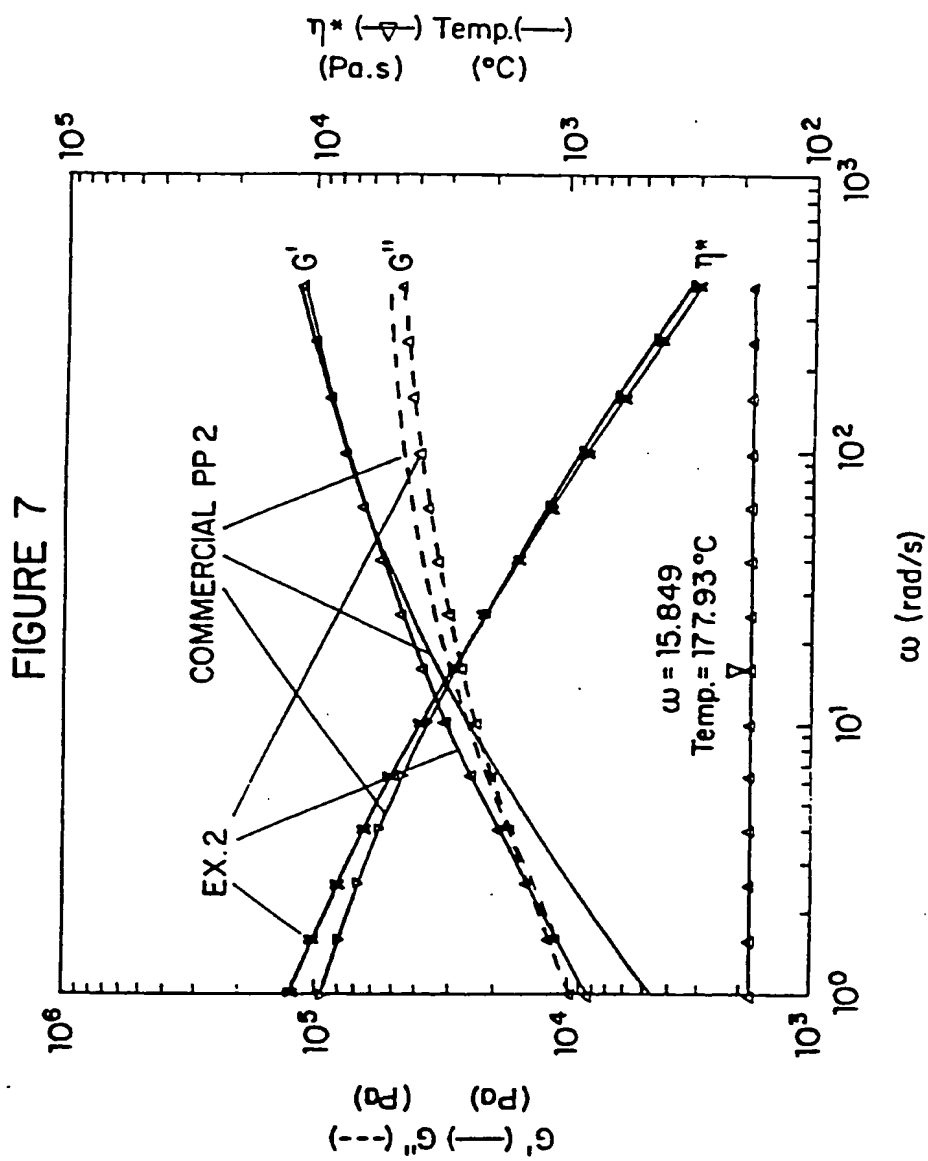
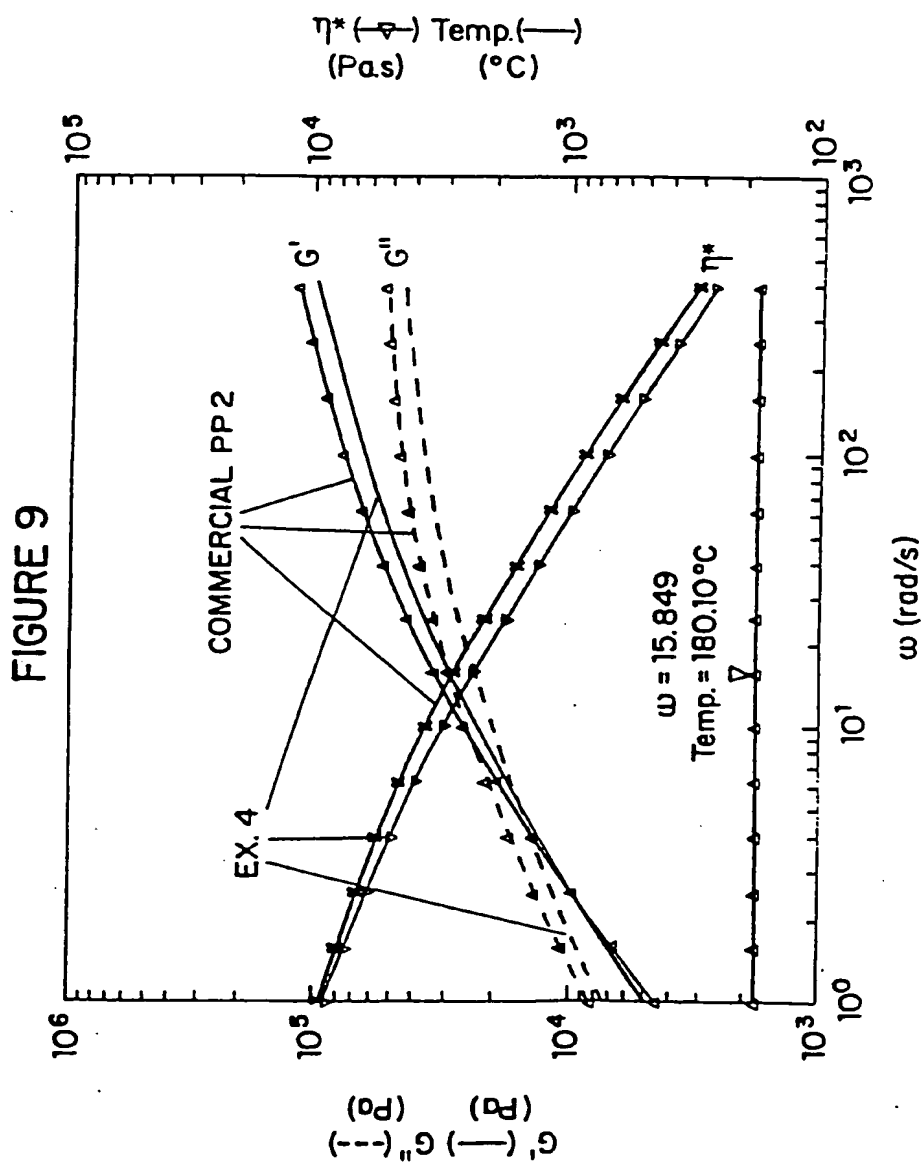


FIGURE 3









INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/BR 94/00019

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO-A-9114718	03-10-91	DE-A- 4009169 AU-A- 7475791	26-09-91 21-10-91
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